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| <p>(54) Title: FUEL ADDITIVE COMPOSITIONS CONTAINING ALIPHATIC AMINES AND POLYALKYL HYDROXYAROMATICS</p> | | |
| <p>(57) Abstract A fuel additive composition comprising: (a) a fuel-soluble aliphatic amine selected from the group consisting of (1) a straight or branched chain hydrocarbyl-substituted amine, (2) a hydroxyalkyl substituted amine, and (3) a straight or branched chain hydrocarbyl-substituted succinimide; and (b) a polyalkyl hydroxyaromatic compound or salt thereof wherein the polyalkyl group has sufficient molecular weight and carbon chain length to render the polyalkyl hydroxyaromatic compound soluble in hydrocarbons boiling in the gasoline or diesel range.</p> | | |

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01 FUEL ADDITIVE COMPOSITIONS CONTAINING
02 ALIPHATIC AMINES
03 AND POLYALKYL HYDROXYAROMATICS
04

05 BACKGROUND OF THE INVENTION
06

07 This invention relates to a fuel additive composition. More
08 particularly, this invention relates to a fuel additive
09 composition containing an aliphatic amine and a polyalkyl
10 hydroxyaromatic compound.
11

12 It is well known in the art that liquid hydrocarbon
13 combustion fuels, such as fuel oils and gasolines, tend to
14 exhibit certain deleterious characteristics, either after
15 long periods of storage or under actual operational
16 conditions. Gasolines, for example, in operational use tend
17 to deposit sludge and varnish at various points in the power
18 system, including the carburetor or injectors and the intake
19 valves. It is desirable, therefore, to find a means for
20 improving liquid hydrocarbon fuels by lessening their
21 tendency to leave such deposits.
22

23 U.S. Patent No. 3,849,085 discloses a motor fuel composition
24 comprising a mixture of hydrocarbon in the gasoline boiling
25 range containing about 0.01 to 0.25 volume percent of a high
26 molecular weight aliphatic hydrocarbon substituted phenol in
27 which the aliphatic hydrocarbon radical has an average
28 molecular weight in the range of about 500 to 3,500. This
29 patent teaches that gasoline compositions containing a minor
30 amount of an aliphatic hydrocarbon substituted phenol not
31 only prevents or inhibits the formation of intake valve and
32 port deposits in a gasoline engine but also enhances the
33 performance of the fuel composition in engines designed to
34 operate at higher operating temperatures with a minimum of

01 decomposition and deposit formation in the manifold of the
02 engine.

03

04 U.S. Patent No. 4,134,846 discloses a fuel additive
05 composition comprising a mixture of (1) the reaction product
06 of an aliphatic hydrocarbon-substituted phenol,
07 epichlorohydrin and a primary or secondary mono- or
08 polyamine, and (2) a polyalkylene phenol. This patent
09 teaches that such compositions show excellent carburetor,
10 induction system and combustion chamber detergency and, in
11 addition, provide effective rust inhibition when used in
12 hydrocarbon fuels at low concentrations.

13

14 U.S. Patent No. 4,231,759 discloses a fuel additive
15 composition comprising the Mannich condensation product of
16 (1) a high molecular weight sulfur-free alkyl-substituted
17 hydroxyaromatic compound wherein the alkyl group has a
18 number average molecular weight of about 600 to 3,000 (2) an
19 amine containing at least one active hydrogen atom, and (3)
20 an aldehyde, wherein the respective molar ratio of reactants
21 is 1:0.1-10 : 0.1-10.

22

23

SUMMARY OF THE INVENTION

24

25 The present invention provides a novel fuel additive
26 composition comprising:

27

28 (a) a fuel-soluble aliphatic amine selected from the group
29 consisting of:

30

31 (1) a straight or branched chain hydrocarbyl-
32 substituted amine having at least one basic
33 nitrogen atom wherein the hydrocarbyl group has a

34

- 01 number average molecular weight of about 250 to
02 3,000,
03
- 04 (2) a hydroxyalkyl-substituted amine comprising the
05 reaction product of (i) a polyolefin epoxide
06 derived from a branched-chain polyolefin having a
07 number average molecular weight of about 250 to
08 3,000, and (ii) a nitrogen-containing compound
09 selected from ammonia, a monoamine having from 1
10 to 40 carbon atoms, and a polyamine having from 2
11 to about 12 amine nitrogen atoms and from 2 to
12 about 40 carbon atoms, and
13
- 14 (3) a straight or branched chain hydrocarbyl-
15 substituted succinimide comprising the reaction
16 product of a straight or branched chain
17 hydrocarbyl-substituted succinic acid or
18 anhydride, wherein the hydrocarbyl group has a
19 number average molecular weight of about 250 to
20 3,000, and a polyamine having from 2 to about 12
21 amine nitrogen atoms and 2 to about 40 carbon
22 atoms; and
23
- 24 (b) a polyalkyl hydroxyaromatic compound or salt thereof
25 wherein the polyalkyl group has sufficient molecular
26 weight and carbon chain length to render the polyalkyl
27 hydroxyaromatic compound soluble in hydrocarbons
28 boiling in the gasoline or diesel range.
29
- 30 The present invention further provides a fuel composition
31 comprising a major amount of hydrocarbons boiling in the
32 gasoline or diesel range and an effective detergent amount
33 of the novel fuel additive composition described above.
34

01 The present invention is also concerned with a fuel
02 concentrate comprising an inert stable oleophilic organic
03 solvent boiling in the range of from about 150°F to 400°F
04 and from about 10 to 70 weight percent of the fuel additive
05 composition of the instant invention.

06
07 Among other factors, the present invention is based on the
08 surprising discovery that the unique combination of an
09 aliphatic amine and a polyalkyl hydroxyaromatic compound
10 provides unexpectedly superior deposit control performance
11 when compared to each component individually.

12

13 DETAILED DESCRIPTION OF THE INVENTION

14

15 The Aliphatic Amine

16

17 As noted above, the fuel-soluble aliphatic amine component
18 of the present fuel additive composition is an amine
19 selected from the group consisting of a straight or branched
20 chain hydrocarbyl-substituted amine, a hydroxyalkyl-
21 substituted amine and a hydrocarbyl-substituted succinimide.
22 Preferably, such aliphatic amines will be of sufficient
23 molecular weight so as to be nonvolatile at normal engine
24 intake valve operating temperatures, which are generally in
25 the range of about 175°C to 300°.

26

27 A. The Hydrocarbyl-Substituted Amine

28

29 The hydrocarbyl-substituted amine employed as the aliphatic
30 amine component of the present fuel additive composition is
31 a straight or branched chain hydrocarbyl-substituted amine
32 having at least one basic nitrogen atom wherein the
33 hydrocarbyl group has a number average molecular weight of
34 about 250 to 3,000.

01 Preferably, the hydrocarbyl group will have a number average
02 molecular weight in the range of about 700 to 2,200, and
03 more preferably, in the range of about 900 to 1,500. The
04 hydrocarbyl group may be either straight chain or branched
05 chain. When the hydrocarbyl group is straight chain, a
06 preferred aliphatic amine is oleyl amine.

07

08 When employing a branched chain hydrocarbyl amine, the
09 hydrocarbyl group is preferably derived from polymers of C₂
10 to C₆ olefins. Such branched-chain hydrocarbyl group will
11 ordinarily be prepared by polymerizing olefins of from 2 to
12 6 carbon atoms (ethylene being copolymerized with another
13 olefin so as to provide a branched-chain). The branched
14 chain hydrocarbyl group will generally have at least 1
15 branch per 6 carbon atoms along the chain, preferably at
16 least 1 branch per 4 carbon atoms along the chain and, more
17 preferably, at least 1 branch per 2 carbon atoms along the
18 chain. The preferred branched-chain hydrocarbyl groups are
19 polypropylene and polyisobutylene. The branches will
20 usually be of from 1 to 2 carbon atoms, preferably 1 carbon
21 atom, that is, methyl. In general, the branched-chain
22 hydrocarbyl group will contain from about 18 to about 214
23 carbon atoms, preferably from about 50 to about 157 carbon
24 atoms.

25

26 In most instances, the branched-chain hydrocarbyl amines are
27 not a pure single product, but rather a mixture of compounds
28 having an average molecular weight. Usually, the range of
29 molecular weights will be relatively narrow and peaked near
30 the indicated molecular weight.

31

32 The amine component of the branched-chain hydrocarbyl amines
33 may be derived from ammonia, a monoamine or a polyamine.

34

01 The monoamine or polyamine component embodies a broad class
02 of amines having from 1 to about 12 amine nitrogen atoms and
03 from 1 to 40 carbon atoms with a carbon to nitrogen ratio
04 between about 1:1 and 10:1. Generally, the monoamine will
05 contain from 1 to about 40 carbon atoms and the polyamine
06 will contain from 2 to about 12 amine nitrogen atoms and
07 from 2 to about 40 carbon atoms. In most instances, the
08 amine component is not a pure single product, but rather a
09 mixture of compounds having a major quantity of the
10 designated amine. For the more complicated polyamines, the
11 compositions will be a mixture of amines having as the major
12 product the compound indicated and having minor amounts of
13 analogous compounds. Suitable monoamines and polyamines are
14 described more fully below in the discussion of
15 hydroxyalkyl-substituted amines.

16
17 When the amine component is a polyamine, it will preferably
18 be a polyalkylene polyamine, including alkylenediamine.
19 Preferably, the alkylene group will contain from 2 to 6
20 carbon atoms, more preferably from 2 to 3 carbon atoms.
21 Examples of such polyamines include ethylene diamine,
22 diethylene triamine, triethylene tetramine and tetraethylene
23 pentamine. Preferred polyamines are ethylene diamine and
24 diethylene triamine.

25
26 A particularly preferred branched-chain hydrocarbyl amine is
27 polyisobutenyl ethylene diamine.

28
29 The branched-chain hydrocarbyl amines employed in the fuel
30 additive composition of the invention are prepared by
31 conventional procedures known in the art. Such branched-
32 chain hydrocarbyl amines and their preparations are
33 described in detail in U.S. Patent Nos. 3,438,757;
34

01 3,565,804; 3,574,576; 3,848,056 and 3,960,515, the
02 disclosures of which are incorporated herein by reference.
03

04 B. The Hydroxyalkyl-Substituted Amine
05

06 The hydroxyalkyl-substituted amine additive employed in the
07 fuel composition of the present invention comprises the
08 reaction product of (a) a polyolefin epoxide derived from a
09 branched chain polyolefin having an average molecular weight
10 of about 250 to 3,000 and (b) a nitrogen-containing compound
11 selected from ammonia, a monoamine having from 1 to 40
12 carbon atoms, and a polyamine having from 2 to about 12
13 amine nitrogen atoms and from 2 to about 40 carbon atoms.
14 The amine component of this reaction product is selected to
15 provide solubility in the fuel composition and deposit
16 control activity.
17

18 Polyolefin Epoxide Component
19

20 The polyolefin epoxide component of the presently employed
21 hydroxyalkyl-substituted amine reaction product is obtained
22 by oxidizing a polyolefin with an oxidizing agent to give an
23 alkylene oxide, or epoxide, in which the oxirane ring is
24 derived from oxidation of the double bond in the polyolefin.
25

26 The polyolefin starting material used in the preparation of
27 the polyolefin epoxide is a high molecular weight branched
28 chain polyolefin having an average molecular weight of about
29 250 to 3,000, preferably from about 700 to 2,200, and more
30 preferably from about 900 to 1,500.
31

32 Such high molecular weight polyolefins are generally
33 mixtures of molecules having different molecular weights and
34 can have at least one branch per 6 carbon atoms along the

01 chain, preferably at least one branch per 4 carbon atoms
02 along the chain, and particularly preferred that there be
03 about one branch per 2 carbon atoms along the chain. These
04 branched chain olefins may conveniently comprise polyolefins
05 prepared by the polymerization of olefins of from 2 to 6
06 carbon atoms, and preferably from olefins of from 3 to 4
07 carbon atoms, and more preferably from propylene or
08 isobutylene. When ethylene is employed, it will normally be
09 copolymerized with another olefin so as to provide a
10 branched chain polyolefin. The addition-polymerizable
11 olefins employed are normally 1-olefins. The branch may be
12 of from 1 to 4 carbon atoms, more usually of from 1 to 2
13 carbon atoms, and preferably methyl.

14

15 In general, any high molecular weight branched chain
16 polyolefin isomer whose epoxide is capable of reacting with
17 an amine is suitable for use in preparing the presently
18 employed fuel additives. However, sterically hindered
19 epoxides, such as tetra-alkyl substituted epoxides, are
20 generally slower to react.

21

22 Particularly preferred polyolefins are those containing an
23 alkylvinylidene isomer present in an amount at least about
24 20%, and preferably at least 50%, of the total polyolefin
25 composition. The preferred alkylvinylidene isomers include
26 methylvinylidene and ethylvinylidene, more preferably the
27 methylvinylidene isomer.

28

29 The especially preferred high molecular weight polyolefins
30 used to prepare the instant polyolefin epoxides are
31 polyisobutenes which comprise at least about 20% of the more
32 reactive methylvinylidene isomer, preferably at least 50%
33 and more preferably at least 70%. Suitable polyisobutenes
34 include those prepared using BF₃ catalysts. The preparation

01 of such polyisobutenes in which the methylvinylidene isomer
02 comprises a high percentage of the total composition is
03 described in U.S. Patent Nos. 4,152,499 and 4,605,808.

04

05 Examples of suitable polyisobutenes having a high
06 alkylvinylidene content include Ultravis 30, a polyisobutene
07 having a molecular weight of about 1300 and a
08 methylvinylidene content of about 76%, available from
09 British Petroleum.

10

11 As noted above, the polyolefin is oxidized with a suitable
12 oxidizing agent to provide an alkylene oxide, or polyolefin
13 epoxide, in which the oxirane ring is formed from oxidation
14 of the polyolefin double bond.

15

16 The oxidizing agent employed may be any of the well known
17 conventional oxidizing agents used to oxidize double bonds.
18 Suitable oxidizing agents include hydrogen peroxide,
19 peracetic acid, perbenzoic acid, performic acid,
20 monoperphthalic acid, percamphoric acid, persuccinic acid
21 and petrifluoroacetic acid. The preferred oxidizing agent
22 is peracetic acid.

23

24 When peracetic acid is used as the oxidizing agent,
25 generally a 40% peracetic acid solution and about a 5%
26 equivalent of sodium acetate (as compared to the peracetic
27 acid) is added to the polyolefin in a molar ratio of per-
28 acid to olefin in the range of about 1.5:1 to 1:1,
29 preferably about 1.2:1. The mixture is gradually allowed to
30 react at a temperature in the range of about 20°C to 90°C.

31

32 The resulting polyolefin epoxide, which is isolated by
33 conventional techniques, is generally a liquid or semi-solid

34

01 resin at room temperature, depending on the type and
02 molecular weight of olefin employed.

03

04 Amine Component

05

06 The amine component of the presently employed hydroxyalkyl-
07 substituted amine reaction product is derived from a
08 nitrogen-containing compound selected from ammonia, a
09 monoamine having from 1 to 40 carbon atoms, and a polyamine
10 having from 2 to about 12 amine nitrogen atoms and from 2 to
11 about 40 carbon atoms. The amine component is reacted with
12 a polyolefin epoxide to produce the hydroxyalkyl-substituted
13 amine fuel additive finding use within the scope of the
14 present invention. The amine component provides a reaction
15 product with, on the average, at least about one basic
16 nitrogen atom per product molecule, i.e., a nitrogen atom
17 titratable by a strong acid.

18

19 Preferably, the amine component is derived from a polyamine
20 having from 2 to about 12 amine nitrogen atoms and from 2 to
21 about 40 carbon atoms. The polyamine preferably has a
22 carbon-to-nitrogen ratio of from about 1:1 to 10:1.

23

24 The polyamine may be substituted with substituents selected
25 from (A) hydrogen, (B) hydrocarbyl groups of from 1 to about
26 10 carbon atoms, (C) acyl groups of from 2 to about 10
27 carbon atoms, and (D) monoketo, monohydroxy, mononitro,
28 monocyano, lower alkyl and lower alkoxy derivatives of (B)
29 and (C). "Lower", as used in terms like lower alkyl or
30 lower alkoxy, means a group containing from 1 to about 6
31 carbon atoms. At least one of the substituents on one of
32 the basic nitrogen atoms of the polyamine is hydrogen, e.g.,
33 at least one of the basic nitrogen atoms of the polyamine is
34 a primary or secondary amino nitrogen.

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01 Hydrocarbyl, as used in describing the amine components of
02 this invention, denotes an organic radical composed of
03 carbon and hydrogen which may be aliphatic, alicyclic,
04 aromatic or combinations thereof, e.g., aralkyl.
05 Preferably, the hydrocarbyl group will be relatively free of
06 aliphatic unsaturation, i.e., ethylenic and acetylenic,
07 particularly acetylenic unsaturation. The substituted
08 polyamines of the present invention are generally, but not
09 necessarily, N-substituted polyamines. Exemplary
10 hydrocarbyl groups and substituted hydrocarbyl groups
11 include alkyls such as methyl, ethyl, propyl, butyl,
12 isobutyl, pentyl, hexyl, octyl, etc., alkenyls such as
13 propenyl, isobutenyl, hexenyl, octenyl, etc., hydroxyalkyls,
14 such as 2-hydroxyethyl, 3-hydroxypropyl, hydroxy-isopropyl,
15 4-hydroxybutyl, etc., ketoalkyls, such as 2-ketopropyl,
16 6-ketooctyl, etc., alkoxy and lower alkenoxy alkyls, such as
17 ethoxyethyl, ethoxypropyl, propoxyethyl, propoxypropyl,
18 diethyleneoxymethyl, triethyleneoxyethyl,
19 tetraethyleneoxyethyl, diethyleneoxyhexyl, etc. The
20 aforementioned acyl groups (C) are such as propionyl,
21 acetyl, etc. The more preferred substituents are hydrogen,
22 C₁-C₆ alkyls and C₁-C₆ hydroxyalkyls.

23

24 In a substituted polyamine, the substituents are found at
25 any atom capable of receiving them. The substituted atoms,
26 e.g., substituted nitrogen atoms, are generally
27 geometrically unequivalent, and consequently the substituted
28 amines finding use in the present invention can be mixtures
29 of mono- and poly-substituted polyamines with substituent
30 groups situated at equivalent and/or unequivalent atoms.

31

32 The more preferred polyamine finding use within the scope of
33 the present invention is a polyalkylene polyamine, including
34 alkylene diamine, and including substituted polyamines,

01 e.g., alkyl and hydroxyalkyl-substituted polyalkylene
02 polyamine. Preferably, the alkylene group contains from 2
03 to 6 carbon atoms, there being preferably from 2 to 3 carbon
04 atoms between the nitrogen atoms. Such groups are
05 exemplified by ethylene, 1,2-propylene, 2,2-dimethyl-
06 propylene, trimethylene, 1,3,2-hydroxypropylene, etc.
07 Examples of such polyamines include ethylene diamine,
08 diethylene triamine, di(trimethylene) triamine, dipropylene
09 triamine, triethylene tetraamine, tripropylene tetraamine,
10 tetraethylene pentamine, and pentaethylene hexamine. Such
11 amines encompass isomers such as branched-chain polyamines
12 and previously-mentioned substituted polyamines, including
13 hydroxy- and hydrocarbyl-substituted polyamines. Among the
14 polyalkylene polyamines, those containing 2-12 amino
15 nitrogen atoms and 2-24 carbon atoms are especially
16 preferred, and the C₂-C₃ alkylene polyamines are most
17 preferred, that is, ethylene diamine, polyethylene
18 polyamine, propylene diamine and polypropylene polyamine,
19 and in particular, the lower polyalkylene polyamines, e.g.,
20 ethylene diamine, dipropylene triamine, etc. A particularly
21 preferred polyalkylene polyamine is diethylene triamine.

22
23 The amine component of the presently employed fuel additive
24 also may be derived from heterocyclic polyamines,
25 heterocyclic substituted amines and substituted heterocyclic
26 compounds, wherein the heterocycle comprises one or more 5-6
27 membered rings containing oxygen and/or nitrogen. Such
28 heterocyclic rings may be saturated or unsaturated and
29 substituted with groups selected from the aforementioned
30 (A), (B), (C) and (D). The heterocyclic compounds are
31 exemplified by piperazines, such as 2-methylpiperazine, N-
32 (2-hydroxyethyl) -piperazine, 1,2-bis-(N-piperazinyl)ethane
33 and N,N'-bis(N-piperazinyl)piperazine, 2-methylimidazoline,
34 3-aminopiperidine, 3-aminopyridine, N-(3-aminopropyl) -

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01 morpholine, etc. Among the heterocyclic compounds the
02 piperazines are preferred.

03

04 Typical polyamines that can be used to form the additives
05 employed in this invention by reaction with a polyolefin
06 epoxide include the following: ethylene diamine,
07 1,2-propylene diamine, 1,3-propylene diamine, diethylene
08 triamine, triethylene tetramine, hexamethylene diamine,
09 tetraethylene pentamine, dimethylaminopropylene diamine,
10 N-(beta-aminoethyl)piperazine, N-(beta-
11 aminoethyl)piperadine, 3-amino-N-ethylpiperidine, N-(beta-
12 aminoethyl) morpholine, N,N'-di(beta-aminoethyl)piperazine,
13 N,N'-di(beta-aminoethyl)imidazolidone-2, N-(beta-cyanoethyl)
14 ethane-1,2-diamine, 1-amino-3,6,9-triazaoctadecane,
15 1-amino-3,6-diaza-9-oxadecane, N-(beta-aminoethyl)
16 diethanolamine, N'-acetylmethyl-N-(beta-aminoethyl) ethane-
17 1,2-diamine, N-acetonyl-1,2-propanediamine, N-(beta-
18 nitroethyl)-1,3-propane diamine, 1,3-dimethyl-5(beta-
19 aminoethyl)hexahydrotriazine, N-(beta-aminoethyl)-
20 hexahydrotriazine, 5-(beta-aminoethyl)-1,3,5-dioxazine, 2-
21 (2-aminoethylamino)ethanol, and 2-(2-(2-aminoethylamino)
22 ethylamino]ethanol.

23

24 Alternatively, the amine component of the presently employed
25 hydroxyalkyl-substituted amine may be derived from an amine
26 having the formula:

27

28

29

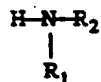
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31

32

33

34



wherein R_1 and R_2 are independently selected from the group
consisting of hydrogen and hydrocarbyl of 1 to about 20
carbon atoms and, when taken together, R_1 and R_2 may form

01 one or more 5- or 6-membered rings containing up to about 20
02 carbon atoms. Preferably, R_1 is hydrogen and R_2 is a
03 hydrocarbyl group having 1 to about 10 carbon atoms. More
04 preferably, R_1 and R_2 are hydrogen. The hydrocarbyl groups
05 may be straight-chain or branched and may be aliphatic,
06 alicyclic, aromatic or combinations thereof. The
07 hydrocarbyl groups may also contain one or more oxygen
08 atoms.

09

10 An amine of the above formula is defined as a "secondary
11 amine" when both R_1 and R_2 are hydrocarbyl. When R_1 is
12 hydrogen and R_2 is hydrocarbyl, the amine is defined as a
13 "primary amine"; and when both R_1 and R_2 are hydrogen, the
14 amine is ammonia.

15

16 Primary amines useful in preparing the fuel additives of the
17 present invention contain 1 nitrogen atom and 1 to about 20
18 carbon atoms, preferably 1 to 10 carbon atoms. The primary
19 amine may also contain one or more oxygen atoms.

20

21 Preferably, the hydrocarbyl group of the primary amine is
22 methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, 2-
23 hydroxyethyl or 2-methoxyethyl. More preferably, the
24 hydrocarbyl group is methyl, ethyl or propyl.

25

26 Typical primary amines are exemplified by N-methylamine, N-
27 ethylamine, N-n-propylamine, N-isopropylamine, N-n-
28 butylamine, N-isobutylamine, N-sec-butylamine, N-tert-
29 butylamine, N-n-pentylamine, N-cyclopentylamine, N-n-
30 hexylamine, N-cyclohexylamine, N-octylamine, N-decylamine,
31 N-dodecylamine, N-octadecylamine, N-benzylamine, N-(2-
32 phenylethyl)amine, 2-aminoethanol, 3-amino-1-propanol, 2-(2-
33 aminoethoxy)ethanol, N-(2-methoxyethyl)amine, N-(2-
34

01 ethoxyethyl)amine and the like. Preferred primary amines
02 are N-methylamine, N-ethylamine and N-n-propylamine.

03
04 The amine component of the presently employed fuel additive
05 may also be derived from a secondary amine. The hydrocarbyl
06 groups of the secondary amine may be the same or different
07 and will generally contain 1 to about 20 carbon atoms,
08 preferably 1 to about 10 carbon atoms. One or both of the
09 hydrocarbyl groups may also contain one or more oxygen
10 atoms.

11
12 Preferably, the hydrocarbyl groups of the secondary amine
13 are independently selected from the group consisting of
14 methyl, ethyl, propyl, butyl, pentyl, hexyl, 2-hydroxyethyl
15 and 2-methoxyethyl. More preferably, the hydrocarbyl groups
16 are methyl, ethyl or propyl.

17
18 Typical secondary amines which may be used in this invention
19 include N,N-dimethylamine, N,N-diethylamine, N,N-di-n-
20 propylamine, N,N-diisopropylamine, N,N-di-n-butylamine, N,N-
21 di-sec-butylamine, N,N-di-n-pentylamine, N,N-di-n-
22 hexylamine, N,N-dicyclohexylamine, N,N-dioctylamine, N-
23 ethyl-N-methylamine, N-methyl-N-n-propylamine, N-n-butyl-N-
24 methylamine, N-methyl-N-octylamine, N-ethyl-N-
25 isopropylamine, N-ethyl-N-octylamine, N,N-di(2-
26 hydroxyethyl)amine, N,N-di(3-hydroxypropyl)amine, N,N-
27 di(ethoxyethyl)amine, N,N-di(propoxyethyl)amine and the
28 like. Preferred secondary amines are N,N-dimethylamine,
29 N,N-diethylamine and N,N-di-n-propylamine.

30
31 Cyclic secondary amines may also be employed to form the
32 additives of this invention. In such cyclic compounds, R₁
33 and R₂ of the formula hereinabove, when taken together, form
34

01 one or more 5- or 6-membered rings containing up to about 20
02 carbon atoms. The ring containing the amine nitrogen atom
03 is generally saturated, but may be fused to one or more
04 saturated or unsaturated rings. The rings may be
05 substituted with hydrocarbyl groups of from 1 to about 10
06 carbon atoms and may contain one or more oxygen atoms.

07
08 Suitable cyclic secondary amines include piperidine, 4-
09 methylpiperidine, pyrrolidine, morpholine, 2,6-
10 dimethylmorpholine and the like.

11
12 In many instances the amine component is not a single
13 compound but a mixture in which one or several compounds
14 predominate with the average composition indicated. For
15 example, tetraethylene pentamine prepared by the
16 polymerization of aziridine or the reaction of
17 dichloroethylene and ammonia will have both lower and higher
18 amine members, e.g., triethylene tetraamine, substituted
19 piperazines and pentaethylene hexamine, but the composition
20 will be mainly tetraethylene pentamine and the empirical
21 formula of the total amine composition will closely
22 approximate that of tetraethylene pentamine. Finally, in
23 preparing the compounds of this invention using a polyamine,
24 where the various nitrogen atoms of the polyamine are not
25 geometrically equivalent, several substitutional isomers are
26 possible and are encompassed within the final product.
27 Methods of preparation of amines and their reactions are
28 detailed in Sidgewick's "The Organic Chemistry of Nitrogen",
29 Clarendon Press, Oxford, 1966; Noller's "Chemistry of
30 Organic Compounds", Saunders, Philadelphia, 2nd Ed., 1957;
31 and Kirk-Othmer's "Encyclopedia of Chemical Technology", 2nd
32 Ed., especially Volume 2, pp. 99-116.

33

34

Preparation of the

01 Hydroxyalkyl-Substituted Amine Reaction Product

02

03 As noted above, the fuel additive finding use in the present
04 invention is a hydroxyalkyl-substituted amine which is the
05 reaction product of (a) a polyolefin epoxide derived from a
06 branched chain polyolefin having an average molecular weight
07 of about 250 to 3,000 and (b) a nitrogen-containing compound
08 selected from ammonia, a monoamine having from 1 to 40
09 carbon atoms, and a polyamine having from 2 to about 12
10 amine nitrogen atoms and from 2 to about 40 carbon atoms.

11

12 The reaction of the polyolefin epoxide and the amine
13 component is generally carried out either neat or with a
14 solvent at a temperature in the range of about 100°C to
15 250°C and preferably from about 180°C to about 220°C. A
16 reaction pressure will generally be maintained in the range
17 from about 1 to 250 atmospheres. The reaction pressure will
18 vary depending on the reaction temperature, presence or
19 absence of solvent and the boiling point of the amine
20 component. The reaction usually is conducted in the absence
21 of oxygen, and may be carried out in the presence or absence
22 of a catalyst. The desired product may be obtained by water
23 wash and stripping, usually by aid of vacuum, of any
24 residual solvent.

25

26 The mole ratio of basic amine nitrogen to polyolefin epoxide
27 will generally be in the range of about 3 to 50 moles of
28 basic amine nitrogen per mole of epoxide, and more usually
29 about 5 to 20 moles of basic amine nitrogen per mole of
30 epoxide. The mole ratio will depend upon the particular
31 amine and the desired ratio of epoxide to amine. Since
32 suppression of polysubstitution of the amine is usually
33 desired, large mole excesses of the amine will generally be
34 used.

01 The reaction of polyolefin epoxide and amine may be
02 conducted either in the presence or absence of a catalyst.
03 When employed, suitable catalysts include Lewis acids, such
04 as aluminum trichloride, boron trifluoride, titanium
05 tetrachloride, ferric chloride, and the like. Other useful
06 catalysts include solid catalysts containing both Brønsted
07 and Lewis acid sites, such as alumina, silica, silica-
08 alumina, and the like.
09
10 The reaction may also be carried out with or without the
11 presence of a reaction solvent. A reaction solvent is
12 generally employed whenever necessary to reduce the
13 viscosity of the reaction product. These solvents should be
14 stable and inert to the reactants and reaction product.
15 Preferred solvents include aliphatic or aromatic
16 hydrocarbons or aliphatic alcohols.
17
18 Depending on the temperature of the reaction, the particular
19 polyolefin epoxide used, the mole ratios and the particular
20 amine, as well as the presence or absence of a catalyst, the
21 reaction time may vary from less than 1 hour to about 72
22 hours.
23
24 After the reaction has been carried out for a sufficient
25 length of time, the reaction mixture may be subjected to
26 extraction with a hydrocarbon-water or hydrocarbon-alcohol-
27 water medium to free the product from any low-molecular
28 weight amine salts which have formed and any unreacted
29 polyamines. The product may then be isolated by evaporation
30 of the solvent.
31
32 In most instances, the additive compositions used in this
33 invention are not a pure single product, but rather a
34 mixture of compounds having an average molecular weight.

01 Usually, the range of molecular weights will be relatively
02 narrow and peaked near the indicated molecular weight.
03 Similarly, for the more complicated amines, such as
04 polyamines, the compositions will be a mixture of amines
05 having as the major product the compound indicated as the
06 average composition and having minor amounts of analogous
07 compounds relatively close in compositions to the dominant
08 compound.

09

10 C. The Hydrocarbyl-Substituted Succinimide

11

12 The hydrocarbyl-substituted succinimide which can be
13 employed as the aliphatic amine component of the present
14 fuel additive composition is a straight or branched chain
15 hydrocarbyl-substituted succinimide comprising the reaction
16 product of a straight or branched chain hydrocarbyl-
17 substituted succinic acid or anhydride, wherein the
18 hydrocarbyl group has a number average molecular weight of
19 about 250 to 3,000, and a polyamine having from 2 to about
20 12 amine nitrogen atoms and 2 to about 40 carbon atoms.

21

22 Preferably, the hydrocarbyl group will have a number average
23 molecular weight in the range of about 700 to 2,200, and
24 more preferably, in the range of about 900 to 1,500. The
25 hydrocarbyl group may be either straight chain or branched
26 chain. Preferably, the hydrocarbyl group will be a branched
27 chain hydrocarbyl group.

28

29 When employing a branched chain hydrocarbyl-substituted
30 succinimide, the branched chain hydrocarbyl group is
31 preferably derived from polymers of C₂ to C₆ olefins. Such
32 branched chain hydrocarbyl groups are described more fully
33 above in the discussion of hydrocarbyl-substituted amines
34 and hydroxyalkyl-substituted amines. Preferably, the

01 branched chain hydrocarbyl group will be derived from
02 polypropylene or polyisobutylene. More preferably, the
03 branched chain hydrocarbyl group will be derived from
04 polyisobutylene.
05

06 The succinimides employed in the present invention are
07 prepared by reacting a straight or branched chain
08 hydrocarbyl-substituted succinic acid or anhydride with a
09 polyamine having from 2 to about 12 amine nitrogen atoms and
10 2 to about 40 carbon atoms.
11

12 Hydrocarbyl-substituted succinic anhydrides are well known
13 in the art and are prepared by the thermal reaction of
14 olefins and maleic anhydride as described, for example, in
15 U.S. Patent Nos. 3,361,673 and 3,676,089. Alternatively,
16 hydrocarbyl-substituted succinic anhydrides can be prepared
17 by reaction of chlorinated olefins with maleic anhydride as
18 described, for example, in U.S. Patent No. 3,172,892. The
19 olefin employed in these reactions has a number average
20 molecular weight in the range of about 250 to about 3,000.
21 Preferably, the number average molecular weight of the
22 olefin is about 700 to about 2,200, more preferably about
23 900 to 1,500.
24

25 The reaction of a polyamine with an alkenyl or alkyl
26 succinic acid or anhydride to produce a polyamino alkenyl or
27 alkyl succinimide is well known in the art and is described,
28 for example, in U.S. Patent Nos. 3,018,291; 3,024,237;
29 3,172,892; 3,219,666; 3,223,495; 3,272,746; 3,361,673 and
30 3,443,918.
31

32 The Amine Component of the Succinimide
33
34

01 The amine moiety of the hydrocarbyl-substituted succinimide
02 is preferably derived from a polyamine having from 2 to
03 about 12 amine nitrogen atoms and from 2 to about 40 carbon
04 atoms. The polyamine is preferably reacted with a
05 hydrocarbyl-substituted succinic acid or anhydride to
06 produce the hydrocarbyl-substituted succinimide fuel
07 additive finding use within the scope of the present
08 invention. The polyamine, encompassing diamines, provides
09 the product succinimide with, on the average, at least about
10 one basic nitrogen atom per succinimide molecule, i.e., a
11 nitrogen atom titratable by strong acid. The polyamine
12 preferably has a carbon-to-nitrogen ratio of from about 1:1
13 to about 10:1. The polyamine may be substituted with
14 substituents selected from hydrogen, hydrocarbyl groups of
15 from 1 to about 10 carbon atoms, acyl groups of from 2 to
16 about 10 carbon atoms, and monoketone, monohydroxy,
17 mononitro, monocyano, alkyl and alkoxy derivatives of
18 hydrocarbyl groups of from 1 to 10 carbon atoms. It is
19 preferred that at least one of the basic nitrogen atoms of
20 the polyamine is a primary or secondary amino nitrogen. The
21 polyamine component employed in the present invention has
22 been described and exemplified more fully in U.S. Patent No.
23 4,191,537.

24
25 Hydrocarbyl, as used in describing the amine components used
26 in this invention, denotes an organic radical composed of
27 carbon and hydrogen which may be aliphatic, alicyclic,
28 aromatic or combinations thereof, e.g., aralkyl.
29 Preferably, the hydrocarbyl group will be relatively free of
30 aliphatic unsaturation, i.e., ethylenic and acetylenic,
31 particularly acetylenic unsaturation. The more preferred
32 polyamine finding use within the scope of the present
33 invention is a polyalkylene polyamine, including
34 alkylenediamine, and including substituted polyamines, e.g.,

01 alkyl and hydroxyalkyl-substituted polyalkylene polyamine.
02 Preferably, the alkylene group contains from 2 to 6 carbon
03 atoms, there being preferably from 2 to 3 carbon atoms
04 between the nitrogen atoms. Examples of such polyamines
05 include ethylenediamine, diethylene triamine, triethylene
06 tetramine, di(trimethylene) triamine, dipropylene triamine,
07 tetraethylene pentamine, etc. Among the polyalkylene
08 polyamines, polyethylene polyamine and polypropylene
09 polyamine containing 2-12 amine nitrogen atoms and 2-24
10 carbon atoms are especially preferred and in particular, the
11 lower polyalkylene polyamines, e.g., ethylenediamine,
12 diethylene triamine, propylene diamine, dipropylene
13 triamine, etc., are most preferred. Particularly preferred
14 polyamines are ethylene diamine and diethylene triamine.

15

16

The Polyalkyl Hydroxyaromatic Compound

17

18 As noted above, the polyalkyl hydroxyaromatic component of
19 the present fuel additive composition is a polyalkyl
20 hydroxyaromatic compound or salt thereof wherein the
21 polyalkyl group has sufficient molecular weight and carbon
22 chain length to render the polyalkyl hydroxyaromatic
23 compound soluble in hydrocarbons boiling in the gasoline or
24 diesel range. As with the aliphatic amine component of the
25 present invention, the polyalkyl hydroxyaromatic compound
26 will preferably be of sufficient molecular weight so as to
27 be nonvolatile at normal engine intake valve operating
28 temperatures, generally in the range of about 175°C to
29 300°C.

30

31 In general, the polyalkyl substituent on the polyalkyl
32 hydroxyaromatic compound will have an average molecular
33 weight in the range of about 400 to 5,000, preferably about
34 400 to 3,000, more preferably from about 600 to 2,000.

01 The polyalkyl-substituted hydroxyaromatic compounds finding
02 use in this invention are derived from hydroxyaromatic
03 hydrocarbons. Such hydroxyaromatic compounds include
04 mononuclear monohydroxy and polyhydroxy aromatic
05 hydrocarbons having 1 to 4, and preferably 1 to 3, hydroxy
06 groups. Suitable hydroxyaromatic compounds include phenol,
07 catechol, resorcinol, hydroquinone, pyrogallol, and the
08 like. The preferred hydroxyaromatic compound is phenol.

09

10 Suitable polyalkyl hydroxyaromatic compounds and their
11 preparation are described, for example, in U.S. Patent
12 Nos. 3,849,085; 4,231,759 and 4,238,628, the disclosures of
13 each of which are incorporated herein by reference.

14

15 The polyalkyl substituent on the polyalkyl hydroxyaromatic
16 compounds employed in the invention may be generally derived
17 from polyolefins which are polymers or copolymers of
18 mono-olefins, particularly 1-mono-olefins, such as ethylene,
19 propylene, butylene, and the like. Preferably, the
20 mono-olefin employed will have 2 to about 24 carbon atoms,
21 and more preferably, about 3 to 12 carbon atoms. More
22 preferred mono-olefins include propylene, butylene,
23 particularly isobutylene, 1-octene and 1-decene.

24 Polyolefins prepared from such mono-olefins include
25 polypropylene, polybutene, especially polyisobutene, and the
26 polyalphaolefins produced from 1-octene and 1-decene.

27

28 The preferred polyisobutenes used to prepare the presently
29 employed polyalkyl hydroxyaromatic compounds are
30 polyisobutenes which comprise at least about 20% of the more
31 reactive methylvinylidene isomer, preferably at least 50%
32 and more preferably at least 70%. Suitable polyisobutenes
33 include those prepared using BF₃ catalysts. The preparation
34 of such polyisobutenes in which the methylvinylidene isomer

01 comprises a high percentage of the total composition is
02 described in U.S. Patent Nos. 4,152,499 and 4,605,808.

03

04 Examples of suitable polyisobutenes having a high
05 alkylvinylidene content include Ultravis 30, a polyisobutene
06 having a molecular weight of about 1300 and a
07 methylvinylidene content of about 74%, available from
08 British Petroleum.

09

10 Numerous methods are known for preparing the polyalkyl
11 hydroxyaromatic compounds used in the present invention and
12 any of these are considered suitable for producing the
13 polyalkyl hydroxyaromatic component of the instant fuel
14 additive composition. One such method involves the reaction
15 of a phenol with an olefin polymer in the presence of an
16 aluminum chloride-sulfuric acid catalyst, as described in
17 U.S. Patent No. 3,849,085. Similarly, U.S. Patent
18 No. 4,231,759 discloses that polyalkyl hydroxyaromatic
19 compounds may be obtained by the alkylation of phenol with
20 polypropylene, polybutylene and other polyalkylene
21 compounds, in the presence of an alkylation catalyst, such
22 as boron trifluoride.

23

24 One preferred method of preparing polyalkyl hydroxyaromatic
25 compounds is disclosed in U.S. Patent No. 4,238,628. This
26 patent teaches a process for producing undegraded alkylated
27 phenols by alkylating, at about 0°C to 60°C, a complex
28 comprising boron trifluoride and phenol with a propylene or
29 higher olefin polymer having terminal ethylene units,
30 wherein the molar ratio of complex to olefin polymer is
31 about 1:1 to 3:1. Preferred olefin polymers include
32 polybutene having terminal ethylene units.

33

34

01 Preferred polyalkyl hydroxyaromatic compounds finding use in
02 the fuel additive composition of the present invention
03 include polypropylene phenol, polyisobutylene phenol, and
04 polyalkyl phenols derived from polyalphaolefins,
05 particularly 1-decene oligomers.
06

07 Polyalkyl phenols, wherein the polyalkyl group is derived
08 from polyalphaolefins, such as 1-octene and 1-decene
09 oligomers, are described in PCT International Patent
10 Application Publication No. WO 90/07564, published July 12,
11 1990, the disclosure of which is incorporated herein by
12 reference. This publication teaches that such polyalkyl
13 phenols may be prepared by reacting the appropriate
14 polyalphaolefin with phenol in the presence of an alkylating
15 catalyst at a temperature of from about 60°C to 200°C,
16 either neat or in an inert solvent at atmospheric pressure.
17 A preferred alkylation catalyst for this reaction is a
18 sulfonic acid catalyst, such as Amberlyst 15®, available
19 from Rohm and Haas, Philadelphia, Pennsylvania.
20

21 Also contemplated for use in the present fuel additive
22 composition are the salts of the polyalkyl hydroxyaromatic
23 component, such as alkali metal, alkaline earth metal,
24 ammonium, substituted ammonium and sulfonium salts.
25 Preferred salts are the alkali metal salts of the polyalkyl
26 hydroxyaromatic compound; particularly the sodium and
27 potassium salts, and the substituted ammonium salts.
28
29
30
31

32 Fuel Compositions
33
34

01 The fuel additive composition of the present invention will
02 generally be employed in a hydrocarbon distillate fuel
03 boiling in the gasoline or diesel range. The proper
04 concentration of this additive composition necessary in
05 order to achieve the desired detergency and dispersancy
06 varies depending upon the type of fuel employed, the
07 presence of other detergents, dispersants and other
08 additives, etc. Generally, however, from 150 to 7500 weight
09 ppm, preferably from 300 to 2500 ppm, of the present
10 additive composition per part of base fuel is needed to
11 achieve the best results.

12
13 In terms of individual components, fuel compositions
14 containing the additive compositions of the invention will
15 generally contain about 50 to 2500 ppm of the aliphatic
16 amine and about 100 to 5000 ppm of the polyalkyl
17 hydroxyaromatic compound. The ratio of polyalkyl
18 hydroxyaromatic to aliphatic amine will generally range from
19 about 0.5 to 10:1, and will preferably be about 2:1 or
20 greater.

21
22 The deposit control additive may be formulated as a
23 concentrate, using an inert stable oleophilic organic
24 solvent boiling in the range of about 150°F to 400°F.
25 Preferably, an aliphatic or an aromatic hydrocarbon solvent
26 is used, such as benzene, toluene, xylene or higher-boiling
27 aromatics or aromatic thinners. Aliphatic alcohols of about
28 3 to 8 carbon atoms, such as isopropanol, isobutylcarbinol,
29 n-butanol and the like, in combination with hydrocarbon
30 solvents are also suitable for use with the detergent-
31 dispersant additive. In the concentrate, the amount of the
32 present additive composition will be ordinarily at least 10%
33 by weight and generally not exceed 70% by weight, preferably
34

-27-

01 10 to 50 weight percent and most preferably from 10 to 25
02 weight percent.

03

04 In gasoline fuels, other fuel additives may also be included
05 such as antiknock agents, e.g., methylcyclopentadienyl
06 manganese tricarbonyl, tetramethyl or tetraethyl lead, or
07 other dispersants or detergents such as various substituted
08 amines, etc. Also included may be lead scavengers such as
09 aryl halides, e.g., dichlorobenzene or alkyl halides, e.g.,
10 ethylene dibromide. Additionally, antioxidants, metal
11 deactivators, pour point depressants, corrosion inhibitors
12 and demulsifiers may be present.

13

14 In diesel fuels, other well-known additives can be employed,
15 such as pour point depressants, flow improvers, cetane
16 improvers, and the like.

17

18 The following examples are presented to illustrate specific
19 embodiments of this invention and are not to be construed in
20 any way as limiting the scope of the invention.

21

22

EXAMPLES

23

24

Example 1

25

26

Preparation of Polyisobutyl Phenol

27

28 To a flask equipped with a magnetic stirrer, reflux
29 condenser, thermometer, addition funnel and nitrogen inlet
30 was added 203.2 grams of phenol. The phenol was warmed to
31 40°C and the heat source was removed. Then,
32 73.5 milliliters of boron trifluoride etherate was added
33 dropwise. 1040 grams of Ultravis 10 polyisobutene
34 (molecular weight 950, 76% methylvinylidene, available from

01 British Petroleum) was dissolved in 1,863 milliliters of
02 hexane. The polyisobutene was added to the reaction at a
03 rate to maintain the temperature between 22-27°C. The
04 reaction mixture was stirred for 16 hours at room
05 temperature. Then, 400 milliliters of concentrated ammonium
06 hydroxide was added followed by 2,000 milliliters of hexane.
07 The reaction mixture was washed with water (3 x 2,000
08 milliliters), dried over magnesium sulfate, filtered and the
09 solvents removed under vacuum to yield 1,056.5 grams of a
10 crude reaction product. The crude reaction product was
11 determined to contain 80% of the desired product by proton
12 NMR and chromatography on silica gel eluting with hexane,
13 followed by hexane: ethylacetate: ethanol (93:5:2).
14
15

16 Example 2

17
18 Engine Test

19
20 A laboratory engine test was used to evaluate both intake
21 valve and combustion chamber deposit performance of the
22 additive composition of the invention. The test engine is a
23 4.3 liter, TBI (throttle body injected), V6 engine
24 manufactured by General Motors Corporation.
25

26 The major engine dimensions are listed below:
27
28

| Table I - Engine Dimensions | |
|-----------------------------|-----------|
| Bore | 10.16 cm |
| Stroke | 8.84 cm |
| Displacement Volume | 4.3 liter |
| Compression Ratio | 9.3:1 |

01 The test procedure involves engine operation for 40 hours
02 (24 hours a day) on a prescribed load and speed schedule
03 representative of typical driving conditions. The cycle for
04 engine operation during the test is as follows:
05

06

07 **Table II - Engine Driving Cycle**

| 08 Step | Mode | Time in Mode [Sec]* | Dynamometer Load [kg] | Engine Speed [RPM] |
|---------|---------------------|---------------------------|--------------------------|--------------------------|
| 11 1 | Idle | 60 | 0 | 800 |
| 12 2 | City Cruise | 150 | 10 | 1,500 |
| 13 3 | Acceleration | 40 | 25 | 2,800 |
| 14 4 | Heavy HWY Cruise | 210 | 15 | 2,200 |
| 15 5 | Light HWY Cruise | 60 | 10 | 2,200 |
| 16 6 | Idle | 60 | 0 | 800 |
| 17 7 | City Cruise | 180 | 10 | 1,500 |
| 18 8 | Idle | 60 | 0 | 800 |

20

21

22 * All steps except step number 3, include a 15 second
23 transition ramp. Step 3 include a 20 second transition
24 ramp.

25
26 All of the test runs were made with the same base gasoline,
27 which was representative of commercial unleaded fuel. The
28 results are set forth in Table III.
29
30
31
32
33
34

| Table III Laboratory Engine Test Results | | | | |
|---|-----------------------|-------|------------------------------------|--|
| Additive | Concentration, ppm | | Intake Valve Deposits, mg | Combustion Chamber Deposits, mg |
| Base Fuel | - | Run 1 | 530 | 1,455 |
| | | Run 2 | 510 | 1,341 |
| | | Avg. | 520 | 1,398 |
| Amine/Neutral Oil ^a | 200/800 | Run 1 | 203 | 2,585 |
| | | Run 2 | 224 | 2,565 |
| | | Avg. | 214 | 2,575 |
| Polyalkyl Phenol ^b | 400 | Run 1 | 90 | 2,190 |
| | | Run 2 | 104 | 2,534 |
| | | Avg. | 97 | 2,362 |
| Amine/Polyalkyl Phenol ^c | 200/400 | Run 1 | 25 | 2,228 |
| | | Run 2 | 67 | 2,121 |
| | | Avg. | 46 | 2,175 |

^a Mixture of 200 ppm polyisobutyl (MW=1300) ethylene diamine and 800 ppm of Chevron 500R neutral oil. The polyisobutyl group was derived from Parapol 1300 polyisobutene.

^b Ultravis 10 polyisobutyl (MW = 950) phenol.

^c Mixture of 200 ppm polyisobutyl (MW = 1300) ethylene diamine and 400 ppm of Ultravis 10 polyisobutyl (MW = 950) phenol.

The results shown in Table III demonstrate that the combination of polyisobutyl phenol and polyisobutyl ethylene diamine has a synergistic effect and gives significantly better intake valve deposit control than either component by itself. Also, the addition of polyisobutyl phenol to the polyisobutyl ethylene diamine reduces the combustion chamber deposit weight compared to the polyisobutyl ethylene diamine alone.

01 WHAT IS CLAIMED IS:

02

03 1. A fuel additive composition comprising:

04

05 (a) A fuel-soluble aliphatic amine selected from the
06 group consisting of:

07

08 (1) A straight or branched chain hydrocarbyl-
09 substituted amine having at least one basic
10 nitrogen atom wherein the hydrocarbyl group
11 has a number average molecular weight of
12 about 250 to 3,000;

13

14 (2) A hydroxyalkyl-substituted amine comprising
15 the reaction product of (i) a polyolefin
16 epoxide derived from a branched-chain
17 polyolefin having a number average molecular
18 weight of about 250 to 3,000, and (ii) a
19 nitrogen-containing compound selected from
20 ammonia, a monoamine having from 1 to 40
21 carbon atoms, and a polyamine having from 2
22 to about 12 amine nitrogen atoms and from 2
23 to about 40 carbon atoms; and

24

25 (3) A straight or branched chain hydrocarbyl-
26 substituted succinimide comprising the
27 reaction product of a straight or branched
28 chain hydrocarbyl-substituted succinic acid
29 or anhydride, wherein the hydrocarbyl group
30 has a number average molecular weight of
31 about 250 to 3,000, and a polyamine having
32 from 2 to about 12 amine nitrogen atoms and 2
33 to about 40 carbon atoms; and

34

- 01 (b) A polyalkyl hydroxyaromatic compound or salt
02 thereof wherein the polyalkyl group has sufficient
03 molecular weight and carbon chain length to render
04 the polyalkyl hydroxyaromatic compound soluble in
05 hydrocarbons boiling in the gasoline or diesel
06 range.
07
- 08 2. The fuel additive composition according the Claim 1,
09 wherein the hydrocarbyl or hydroxyalkyl substituent on
10 the aliphatic amine of component (a) has a number
11 average molecular weight of about 700 to 2,200.
12
- 13 3. The fuel additive composition according to Claim 2,
14 wherein the hydrocarbyl or hydroxyalkyl substituent on
15 the aliphatic amine of component (a) has a number
16 average molecular weight of about 900 to 1,500.
17
- 18 4. The fuel additive composition according to Claim 1,
19 wherein the aliphatic amine of component (a) is a
20 straight or branched chain hydrocarbyl-substituted
21 amine.
22
- 23 5. The fuel additive composition accord to Claim 4,
24 wherein the aliphatic amine of component (a) is a
25 branched chain hydrocarbyl-substituted amine.
26
- 27 6. The fuel additive composition according to Claim 5,
28 wherein the aliphatic amine of component (a) is a
29 polyisobutyl amine.
30
- 31 7. The fuel additive composition according to Claim 4,
32 wherein the amine moiety of the aliphatic amine is
33 derived from a polyamine having from 2 to 12 amine
34 nitrogen atoms and from 2 to 40 carbon atoms.

-33-

- 01 8. The fuel additive composition according to claim 7,
02 wherein the polyamine is a polyalkylene polyamine
03 having 2 to 12 amine nitrogen atoms and 2 to 24 carbon
04 atoms.
05
- 06 9. The fuel additive composition according to Claim 8,
07 wherein the polyalkylene polyamine is selected from the
08 group consisting of ethylene diamine, diethylene
09 triamine, triethylene tetramine and tetraethylene
10 pentamine.
11
- 12 10. The fuel additive composition according to Claim 9,
13 wherein the polyalkylene polyamine is ethylene diamine
14 or diethylene triamine.
15
- 16 11. The fuel additive composition according to Claim 1,
17 wherein the aliphatic amine of component (a) is a
18 hydroxyalkyl-substituted amine.
19
- 20 12. The fuel additive composition according to Claim 11,
21 wherein the hydroxyalkyl-substituted amine is derived
22 from a branched chain polyolefin selected from
23 polypropylene or polyisobutene.
24
- 25 13. The fuel additive composition according to Claim 12,
26 wherein the branched chain polyolefin is polyisobutene.
27
- 28 14. The fuel additive composition according to Claim
29 11, wherein the hydroxyalkyl-substituted amine is
30 derived from a polyamine having from 2 to about 12
31 amine nitrogen atoms and 2 to about 40 carbon atoms.
32
- 33 15. The fuel additive composition according to Claim 14,
34 wherein the polyamine is a polyalkylene polyamine

01 wherein the alkylene group contains from 2 to 6 carbon
02 atoms and the polyalkylene polyamine contains from 2 to
03 12 nitrogen atoms and from 2 to 24 carbon atoms.

04

05 16. The fuel additive composition according to Claim 15,
06 wherein the polyalkylene polyamine is selected from the
07 group consisting of ethylene diamine, polyethylene
08 polyamine, propylene diamine and polypropylene
09 polyamine.

10

11 17. The fuel additive composition according to Claim 1,
12 wherein the aliphatic amine of component (a) is a
13 straight or branched chain hydrocarbyl-substituted
14 succinimide.

15

16 18. The fuel additive composition according to Claim 17,
17 wherein the aliphatic amine is a branched chain
18 hydrocarbyl-substituted succinimide.

19

20 19. The fuel additive composition according to Claim 18,
21 wherein the branched chain hydrocarbyl substituent is
22 polyisobutyl.

23

24 20. The fuel additive composition according to Claim 17,
25 wherein the hydrocarbyl-substituted succinimide is
26 derived from a polyalkylene polyamine having 2 to 12
27 amine nitrogen atoms and 2 to 24 carbon atoms.

28

29 21. The fuel additive composition according to Claim 20,
30 wherein the polyalkylene polyamine is selected from the
31 group consisting of ethylene diamine, diethylene
32 triamine, triethylene tetramine and tetraethylene
33 pentamine.

34

- 01 22. The fuel additive composition according to Claim 21,
02 wherein the polyalkylene polyamine is ethylene diamine
03 or diethylene triamine.
04
- 05 23. The fuel additive composition according to Claim 1,
06 wherein the polyalkyl hydroxyaromatic compound of
07 component (b) has a polyalkyl group with an average
08 molecular weight of about 400 to 5,000.
09
- 10 24. The fuel additive composition according to Claim 1,
11 wherein the hydroxyaromatic compound is phenol.
12
- 13 25. The fuel additive composition according to Claim 1,
14 wherein the polyalkyl substituent in component (b) is
15 derived from polypropylene, polybutylene, or
16 polyalphaolefin oligomers of 1-decene.
17
- 18 26. The fuel additive composition according to Claim 25,
19 wherein the polyalkyl substituent in component (b) is
20 derived from polyisobutylene.
21
- 22 27. The fuel additive composition according to Claim 26,
23 wherein the polyisobutylene contains at least about 20%
24 of a methylvinylidene isomer.
25
- 26 28. The fuel additive composition according to Claim 1,
27 wherein component (a) is a polyisobutyl amine, wherein
28 the amine moiety is derived from ethylene diamine or
29 diethylene triamine, and component (b) is a
30 polyisobutyl phenol.
31
- 32 29. A fuel composition comprising a major amount of
33 hydrocarbons boiling in the gasoline or diesel range
34

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- 01 and an effective detergent amount of an additive
02 composition comprising:
03
- 04 (a) A fuel-soluble aliphatic amine selected from the
05 group consisting of
06
- 07 (1) A straight or branched chain hydrocarbyl-
08 substituted amine having at least one basic
09 nitrogen atom wherein the hydrocarbyl group
10 has a number average molecular weight of
11 about 250 to 3,000;
12
- 13 (2) A hydroxyalkyl-substituted amine comprising
14 the reaction product of (i) a polyolefin
15 epoxide derived from a branched-chain
16 polyolefin having a number average molecular
17 weight of about 250 to 3,000, and (ii) a
18 nitrogen-containing compound selected from
19 ammonia, a monoamine having from 1 to 40
20 carbon atoms, and a polyamine having from 2
21 to about 12 amine nitrogen atoms and from 2
22 to about 40 carbon atoms; and
23
- 24 (3) A straight or branched chain hydrocarbyl-
25 substituted succinimide comprising the
26 reaction product of a straight or branched
27 chain hydrocarbyl-substituted succinic acid
28 or anhydride, wherein the hydrocarbyl group
29 has a number average molecular weight of
30 about 250 to 3,000, and a polyamine having
31 from 2 to about 12 amine nitrogen atoms and 2
32 to about 40 carbon atoms; and
33
34

- 01 (b) a polyalkyl hydroxyaromatic compound or salt
02 thereof wherein the polyalkyl group has sufficient
03 molecular weight and carbon chain length to render
04 the polyalkyl hydroxyaromatic compound soluble in
05 hydrocarbons boiling in the gasoline or diesel
06 range.
07
- 08 30. A fuel concentrate comprising an inert stable
09 oleophilic organic solvent boiling in the range of from
10 about 150°F to 400°F and from about 10 to 70 weight
11 percent of an additive composition comprising:
12
- 13 (a) A fuel-soluble aliphatic amine selected from the
14 group consisting of
15
- 16 (1) A straight or branched chain hydrocarbyl-
17 substituted amine having at least one basic
18 nitrogen atom wherein the hydrocarbyl group
19 has a number average molecular weight of
20 about 250 to 3,000;
21
- 22 (2) A hydroxyalkyl-substituted amine comprising
23 the reaction product of (i) a polyolefin
24 epoxide derived from a branched-chain
25 polyolefin having a number average molecular
26 weight of about 250 to 3,000, and (ii) a
27 nitrogen-containing compound selected from
28 ammonia, a monoamine having from 1 to 40
29 carbon atoms, and a polyamine having from 2
30 to about 12 amine nitrogen atoms and from 2
31 to about 40 carbon atoms; and
32
- 33 (3) A straight or branched chain hydrocarbyl-
34 substituted succinimide comprising the

01 reaction product of a straight or branched.
02 chain hydrocarbyl-substituted succinic acid
03 or anhydride, wherein the hydrocarbyl group
04 has a number average molecular weight of
05 about 250 to 3,000, and a polyamine having
06 from 2 to about 12 amine nitrogen atoms and 2
07 to about 40 carbon atoms; and
08

09 (b) a polyalkyl hydroxyaromatic compound or salt
10 thereof wherein the polyalkyl group has sufficient
11 molecular weight and carbon chain length to render
12 the polyalkyl hydroxyaromatic compound soluble in
13 hydrocarbons boiling in the gasoline or diesel
14 range.
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US93/12555

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : C10L 1/18, 1/22, 10/00

US CL : 44/347, 412, 432, 433, 434, 450

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 44/347, 412, 432, 433, 434, 450

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| Y | US, A, 3,849,085 (KREUZ ET AL.) 19 NOVEMBER 1974, (SEE ENTIRE DOCUMENT) | 1-30 |
| Y | US, A, 4,123,232 (FROST, JR.) 31 OCTOBER 1978, (COLUMN 1, LINES 30-37, COLUMN 4, LINES 50-52) | 1-16, 23-30 |
| P,Y | US, A, 5,192,335 (CHERPECK) 09 MARCH 1993, (SEE ABSTRACT) | 1-30 |
| Y | US, A, 5,114,435 (ABRAMO ET AL.) 19 MAY 1992 (COLUMN 2, LINES 33-44; COLUMN 2, LINE 48 TO COLUMN 3, LINE 62) | 1-10, 17-30 |
| Y | UK, A, 2,156,848 A (EXXON RESEARCH AND ENGINEERING COMPANY) 16 OCTOBER 1985 (SEE ENTIRE DOCUMENT) | 1-30 |

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

| | | |
|--|------|--|
| * Special categories of cited documents: | * T | later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention |
| * A* document defining the general state of the art which is not considered to be of particular relevance | * X* | document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone |
| * E* earlier document published on or after the international filing date | * Y* | document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art |
| * L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) | * A* | document member of the same patent family |
| * O* document referring to an oral disclosure, use, exhibition or other means | | |
| * P* document published prior to the international filing date but later than the priority date claimed | | |

Date of the actual completion of the international search

17 March 1994

Date of mailing of the international search report

30 MAR 1994

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231Authorized officer

JERRY D. JOHNSON

Facsimile No. NOT APPLICABLE

Telephone No. (703) 308-0661

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/12555

| C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|---|--|-----------------------|
| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| A | US, A, 3,438,757 (HONNEN ET AL.) 15 APRIL 1969 | |
| A | US, A, 4,832,702 (KUMMER ET AL.) 23 MAY 1989 | |